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Cuboctahedral and Icosahedral Bonding

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CUBOCTAHEDRAL AND ICOSAHEDRAL BONDING

BY

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CUBOCTAHEDRAL AND ICOSAHEDRAL BONDING

This thesis is approved as a creditable, independent investigation by a candidate for the degree, Master of Science, and acceptable as meeting the thesis requirements for this degree; but without implying that the conclusions reached by the candidate are necessarily the conclusions of the major department.

Thesis Advisor

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2441

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J. R. C.

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INTRODUCTION

Before quantum mechanics was developed, the theory of chemical bonding was generally discussed only qualitatively. Since then, however, several theories based on quantitative studies have been advanced.

Even the use of quantum mechanics makes it possible to get exact results for only the simplest problems. Nevertheless, quantitative results can be obtained for the n-body problem by using approximation methods.

The use of group theory in chemical bonding, first proposed by Bethe, simplified the problem a great deal. This allows one to take advantage of the symmetry properties of a molecule or ion in determining the bonding wave functions and energy levels.

The two most widely accepted methods of applying group theory and quantum mechanics to chemical bonding have been employed here to determine the bonding wave functions and energy levels in the cuboctahedral and icosahedral structures.

The directed valence method developed by Heitler, London, Pauling, and Slater has been employed to determine the wave functions involved in central atom bonding in the cuboctahedral structure. This method is characterized by the "hybrid" orbitals formed from linear combinations of the atomic orbitals of the central atom. The strength of these bonds are calculated and compared with those of the

icosahedral structure. The π bonds which could be formed in this structure are also discussed briefly.

The molecular orbital method due to Lennard-Jones, Hund, and Mulliken is used to find the molecular orbitals and energy levels involved in bonding in both the cuboctahedral and icosahedral structures. In this method the bonding orbitals are considered to extend over the whole molecule, and they are formed from linear combinations of atomic orbitals of all the atoms involved.

The difficulties encountered in applying the latter method to the icosahedral structure are discussed briefly, and other possible methods for obtaining a solution are suggested.

GROUP THEORY

The application of quantum mechanics to the theory of chemical bonding has met with considerable success. However, since the Schrödinger equation can be solved exactly in only a few simple cases, we are generally limited to approximate methods of solution. Fortunately, there is a certain class of results which depends only on the symmetry properties of the system; and these results can be obtained by use of group theory.

Since elementary knowledge of group theory will be assumed, only a general discussion of the theory applicable to the problem will follow.

A polyatomic molecule can be classified as belonging to a particular symmetry group if only like particles are interchanged under the operations of that group. These operations, of course, must satisfy the group requirements.

A representation of a group is a set of elements which is, in general, homomorphic (a many-to-one correspondence between original group and representation group) to the group. Any symmetry group can be represented by matrices, and this is the only type of representation which will be considered in this application.

Thus, a representation of the group of operations $A_1, A_2, A_3, \cdots, A_n$ are the square matrices $(A_1), (A_2), (A_3), \cdots, (A_n)$, if $(A_i)(A_j)=(A_k)$ when $A_iA_j=A_k$ for all

of the matrices. The representation is faithful if all of the matrices corresponding to the operations are different. If some of the matrices are the same, the representation is unfaithful. The simplest representation of a group is the one in which each element of the group is represented by the one-dimensional unit matrix. The dimension of a representation is the number of rows and columns in the matrices.

An important representation in this application is that which represents the permutations of the vertices of the geometrical figure under the operations of the group. A permutation matrix is a square matrix in which each row and column contains all zeros except one entry which is unity. The symbols representing the n vertices can be thought of as the components of a n-dimensional vector. Then the operations of the group will change this vector into another n-dimensional vector with the same components only in a different order. The identity operation is represented by the n x n unit matrix since all of the diagonal terms must be unity. This matrix will have a character equal to the number of vertices. The character is equal to the sum of the diagonal elements and will be discussed in more detail later. The other operations will be represented by matrices which have characters equal to the number of vertices which remain unchanged under the particular operation. Only for these vertices will the unity remain on

the diagonal; all others will be moved to some other position in the row or column.

There is an infinite number of reducible representations for each group, but they are all built up from a relatively few irreducible representations. The number of nonequivalent irreducible representations for any group is equal to the number of classes in the group.[1] Two representations are equivalent if one can be transformed into the other by operating on every matrix in the representation by the same similarity transformation.

A n-dimensional representation is reducible if a matrix S can be found such that the similarity transformation $S^{-1}(A_i)S$ will reduce every matrix (A_i) of the representation to the form

$$\begin{pmatrix} (A_i)_1 & 0 \\ 0 & (A_i)_2 \end{pmatrix}$$

where $(A_i)_1$ is of order m, $(A_i)_2$ is of order (n-m), and m<n. Then $(A_i)_1$ and $(A_i)_2$ are examined to see if they are reducible, continuing the process until (A_i) is completely reduced. When this is accomplished, the set of irreducible matrices which occupy corresponding places on the diagonals of the reducible matrices form an irreducible representation which shall be represented by Γ_i.

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[1] Bryan Higman, Applied Group-Theoretic and Matrix Methods, p. 48, Oxford at the Clarendon Press: London, 1955.

It is possible that a certain irreducible representation Γ^i of the group may appear more than once or not at all when a particular reducible representation is reduced. This can be indicated by writing the reducible representation Γ in the form

$$\Gamma = c_1\Gamma^1 + c_2\Gamma^2 + \cdots + c_s\Gamma^s \qquad (1)$$

where s is the number of classes in the group and the c's are positive integers or zero. This notation, called the direct sum, does not indicate that the representations are added, but only that the matrices (A_i) have been reduced to this form.

If the representations of the group consist of unitary or orthogonal matrices (since we are dealing with real matrices, an orthogonal matrix is unitary); it can be shown that the irreducible representations will be orthogonal.[2] This can be written as

$$\sum_A A^j_{kl}\, A^{i*}_{mn} = \frac{g}{(d_i d_j)^{1/2}}\, \delta_{ij}\, \delta_{km}\, \delta_{in} \qquad (2)$$

where d_i is the dimension of the ith irreducible representation, g is the order of the group, the asterisk indicates the complex conjugate, and the summation is over all of the operations of the group. It will be assumed that all of the representations do consist of orthogonal matrices. It

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[2] Eugene P. Wigner, Group Theory , p. 83, Academic Press: New York and London, 1959.

can also be shown[3] that

$$d_1^2 + d_2^2 + \cdots + d_s^2 = g \qquad (3)$$

The set of d's which will satisfy this equation for symmetry groups is unique.

If all of the irreducible representations do not appear in the reduction of the set of (A_i) matrices considered, then another reducible representation must be reduced until the total number of irreducible representations of the proper dimensions are obtained.

Usually the process of finding all of the irreducible representations of a group is tedious. It is often difficult to find the proper matrix S which will reduce a particular reducible representation. Fortunately in many physical applications, it is sufficient to know the character of the matrices of the irreducible representations. The character was mentioned previously and will now be discussed in more detail.

It is sufficient to work with the characters of the matrices because there is a one-to-one correspondence between the character system of a group and its irreducible representations. This correspondence will be more apparent if some of their properties are discussed.

The character will be represented by $\chi^j(A)$; where A is the operation, and j is the particular irreducible repre-

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[3] Ibid., p. 115.

sentation. The characters representing elements of the same class are identical. This can be explained by the fact that any element in a class may be obtained from another element of the class by a similarity transformation, and it can be shown that the sum of the diagonal elements of a matrix does not change under this type of transformation.[4] This is one of the advantages of considering the characters rather than the irreducible representations. It is often difficult to determine whether or not a particular irreducible representation is equivalent to another of the same dimension, since it is difficult to find the matrix which will transform one into the other under a similarity transformation. On the other hand, if the characters of two irreducible representations are the same, it is a sufficient condition for their equivalence.[5]

The identity operation E is always represented by the unit matrix. Therefore, the character of the matrix representing this operation will be equal to the dimension of the representation.

From equation (3) it is obvious that

$$[\chi^1(E)]^2 + [\chi^2(E)]^2 + \cdots + [\chi^s(E)]^2 = g \qquad (4)$$

which can be written as

$$\sum_{i=1}^{s} [\chi^i(E)]^2 = g \qquad (5)$$

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[4] Ibid., p. 9.

[5] Ibid., p. 86.

The characters, as well as the irreducible representations, form an orthogonal system.[6] This property of the character can be expressed as

$$\sum_{A} \chi^{j}(A)\,\chi^{i}(A) = g\,\delta_{ij} \tag{6}$$

where the summation is over all of the operations of the group.

The character $\chi(A)$ of the matrix representing a particular operation A of a reducible representation is given by

$$\chi(A) = \sum_{j=1}^{s} a^{j}\chi^{j}(A) \tag{7}$$

which is analogous to equation (1).

This relation and the orthogonality condition (6) can be used to show that[7]

$$a^{j} = \frac{1}{g} \sum_{i=1}^{s} h_{i}\,\chi(c_{i})\,\chi^{j}(c_{i}) \tag{8}$$

where $\chi(c_1)$ is the character of the ith class of the reducible representation, $\chi^{j}(c_1)$ is the character of the ith class of the jth irreducible representation, and h_1 is the number of elements in the ith class. The last two expressions make it simple to break a reducible representation down into its irreducible components. The importance of these properties of the character will become more clear when applied to a specific structure.

There are different ways to find the characters of

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[6] Ibid., p. 83.

[7] Ibid., p. 86.

a group. In many cases the properties of the character just discussed are all that is necessary to find all of the characters. For other methods of obtaining the characters, reference should be made to texts on group theory.

Since there are only as many irreducible representations as there are classes in a group, the characters can be arranged in a square $s \times s$ table. This is called a character table. Character tables for the more common groups are available in texts; but as mentioned above, there are several methods by which these tables can be determined.

The value of the character table will become more obvious after a discussion of the relationship between group theory and quantum mechanics.

It was implied previously that group theory could be applied in quantum mechanics, but it was not discussed at all. It would be desirable at this point to consider this matter in some detail.

Consider the Schrödinger equation

$$H\Psi = E\Psi \tag{9}$$

for a polyatomic molecule, where Ψ is the wave function of the system with the eigenvalue E. Let R be some operation of the symmetry group of the molecule, so that it has only the effect of interchanging like particles. The symmetry operations can be thought of as simply a renumbering of the like particles. Operate on both sides of the equation

with R:

$$RH\Psi = RE\Psi \tag{10}$$

Since R only interchanges like particles, the energy of the system will not be changed and RH=HR. The operator R also commutes with the scalar quantity E so that

$$HR\Psi = ER\Psi \tag{11}$$

and $R\Psi$ is also a solution of the Schrödinger equation with the eigenvalue E.

If E is a non-degenerate eigenvalue, only Ψ or constant multiples of Ψ will satisfy equation (11). Therefore $R\Psi = c\Psi$ where c is a constant. In order that both Ψ and $R\Psi$ be normalized, c^2 must equal one, so that $c = \pm 1$.

However, if E is k-fold degenerate, then any linear combination of the wave functions $\psi_1, \psi_2, \cdots, \psi_k$ which satisfy the Schrödinger equation will be a solution of equation (11). This can be expressed in the form

$$R\psi_l = \sum_{j=1}^{k} \psi_j A_{jl} \tag{12}$$

where $\sum_{j=1}^{k} A_{jl}^2 = 1$, that is, all of the ψ_j are normalized.

A_{jl} can be considered as the element of a matrix. Since the summation is over j, the ψ_j elements form a row matrix, and the A_{jl} elements form a column matrix. However, if the operation is applied to all k functions of the degenerate set, (A) will be a $\underline{k} \times \underline{k}$ square matrix. This is true because operating on k linearly independent functions will yield k linearly independent combinations of these functions.

Similarly,

$$S\psi_i = \sum_{i=1}^{k} \psi_i B_{ij} \tag{13}$$

where S is another operation of the group. If the operation S is applied to equation (12) then

$$SR\psi_l = \sum_{j=1}^{k} S\psi_j A_{jl} = \sum_{j=1}^{k} \sum_{i=1}^{k} \psi_i B_{ij} A_{jl} \tag{14}$$

If the product of S and R is T, then the above expression can be written as

$$T\psi_l = \sum_{i=1}^{k} \psi_i C_{il} \tag{15}$$

where

$$C_{il} = \sum_{j=1}^{k} B_{ij} A_{jl} \tag{16}$$

It should be noted above that the operation which is performed first and it s corresponding matrix are always on the right.

The matrices (A), (B), (C), • • • form an irreducible representation of the group of operations S, R, T, • • • • The eigenfunctions $\psi_1, \psi_2, \cdots, \psi_k$ are said to form a basis for this irreducible representation since the representation is a result of operating on these functions with the operations of the group. In general, eigenfunctions which have the same eigenvalue form a basis for an irreducible representation except in the case of accidental degeneracy (where eigenfunctions have the same eigenvalue although they behave differently under the operations of the group).

It should be mentioned that the order of degeneracy of a set of atomic orbitals with a given quantum number will generally change when free atoms are combined into

molecules. The field of the other atoms will cause splitting of the energy levels of a particular degenerate set. These smaller sets will each consist of the orbitals which transform in the same manner under the operations of the group. The splitting will, of course, be different for different symmetries.

It is evident now that a number of important results can be obtained without having to solve the Schrödinger equation for a molecule. It was shown previously that the number and dimensions of the irreducible representations can be determined by the use of group theory. Since the dimension of the irreducible representations is equal to the number of linearly independent wave functions, it is also equal to the degeneracy of the set. It is quite easy to obtain the irreducible components of a reducible representation which corresponds to a particular type of bond. From the information above, the eigenfunctions which are available to form these bonds can be obtained since they form bases for the irreducible representations contained in the reducible representation. This particular information is very important in this application. Other properties of the bonding functions must be considered in order to determine the manner in which these eigenfunctions combine. This problem will be discussed later.

For more information concerning applications of group theory to chemical bonding, reference should be made to

texts[9,10,11,12] and articles[13,14] concerned with this problem.

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[9] Margenau and Murphy, The Mathematics of Physics and Chemistry, pp. 548-86, D. Van Nostrand Company, Inc.: Princeton, 1943.

[10] Eyring, Walter, and Kimball, Quantum Chemistry, John Wiley and Sons, Inc.: New York, 1944.

[11] J.S. Lomont, Applications of Finite Groups, Academic Press: New York and London, 1959.

[12] Gerhard Herzberg, Molecular Spectra and Molecular Structure, D. Van Nostrand Company, Inc.: New York, 1945.

[13] H. Bethe, Ann. d. Phys. 3, 133, 1929.

[14] H.E. Rosenthal and G.M. Murphy, Rev. Mod. Phys. 8, 317, 1936.

TYPES OF BONDING

Quantum mechanics has made it possible to write an equation (Schrödinger's equation) for any system of nuclei and electrons. The solution of this equation would provide complete information about the stability, spatial arrangement of nuclei, and other properties of the molecule. However, the n-body problem is so complex that integration of the Schrödinger equation to give good quantitative results has been possible with only the hydrogen molecule. In order to obtain quantitative information about more complicated molecules, it is necessary to use as many methods of approximation as possible.

Two chief methods have been particularly developed in applying quantum mechanics to the problems of valence. One is the theory of directed valence based on the method of localized pairs developed by Heitler, London, Pauling, and Slater (HLPS). The other is the molecular orbital method due to Lennard-Jones, Hund, Mulliken and others. These two methods are different approximations to the solution of a complicated secular equation. A molecular orbital, like an atomic orbital, is a wave function which is a function of the coordinates of only one electron. The wave function is complicated by the fact that more than one atom is involved, and in general the wave function extends over the entire molecule. The molecular orbital method permits the factorization of an n-electron problem

into n one-electron problems, and represents the wave function of the system as a product of their n one-electron wave functions. However, it does not adequately take into account the electron repulsion.

The directed valence method is characterized by "hybrid" orbitals which are formed from linear combinations of atomic orbitals of the central atom to give the desired directional property to the bonding functions. This method too fully recognizes the electron repulsion mentioned above. A brief discussion of both methods will follow, but no attempt will be made to discuss all of the necessary refinements required in both theories in order that they precisely describe the bonding.

The directed valence method consists of finding the proper linear combinations of the s, p, d, and f atomic orbitals of the central atom so that they will project in the direction of the attached atoms. Electrons occupying these orbitals will form covalent bonds with the unpaired electrons in the orbitals of the attached atom lying in the same direction as the "hybrid" orbitals. The more these orbitals overlap, the stronger the resulting bonds. If all of the attached atoms are identical and located symmetrically about the central atom, as in this application, all of the directed orbitals will be equivalent; that is, they will differ from each other only in direction.

It is most convenient to use group theory in con-

structing these orbitals. This was discussed briefly in the section on group theory. The "hybrid" orbitals are acted on by the operations of the symmetry group of the molecule; and a reducible representation, which will be called a σ representation, is obtained. This representation is then broken down into its irreducible components by the method discussed previously. The atomic orbitals of the central atom are then operated on by these operations to determine for which irreducible representations they form bases. Only the orbitals which form bases for the irreducible representations of the reducible representation can be used to form the "hybrid" orbitals. The method for determining the precise manner in which they combine will be discussed in detail for the cuboctahedral structure later.

In the directed valence method only the orbitals of the central atom were used to construct the "hybrid" orbitals. In the molecular orbital method the orbitals of the attached atoms are also considered. The simplest approach, although not the most precise, is simply to use linear combinations of the atomic orbitals (LCAO) to form molecular orbitals. In general, these molecular orbitals extend over the whole molecule rather than between only two atoms as in the directed valence method. However, a number of the molecular orbitals may be found to be concentrated around particular atoms in the molecule. These orbitals form the

inner shells of the molecule and play no essential part in the bonding. They will resemble the inner shell atomic orbitals of the free atoms although they will be distorted due to the fields of the other atoms. In spite of this distortion, most molecular orbital methods consider the inner shell electrons as being in free atomic orbitals.

Electrons are assigned to orbitals in the molecule in the same manner as they are assigned to atomic orbitals of free atoms. Each electron is assigned to a one-electron wave function or orbital which is analogous to an atomic orbital.

The wave functions for this central atom problem were determined by the directed valence method. It would be of some interest at this point to consider how a set of molecular orbitals could be constructed for this type of problem. Consider a wave function $\psi(\Gamma)$ of the central atom which transforms under the operations of the group in a manner corresponding to some irreducible representation. Let ψ_i be a wave function of the ith attached atom. It is assumed that only one orbital of each attached atom need be considered, and that each of these will be symmetric about the line joining this atom with the central one. The LCAO method constructs wave functions of the form

$$\Psi = \psi(\Gamma) + \sum_i a_i \psi_i \qquad (17)$$

The coefficients a_i must be chosen so that the $\sum_i a_i \psi_i$ transform in a manner corresponding to the Γ irreducible

representation. This makes it necessary to determine for which irreducible representations the linear combinations of ψ_i form bases. To accomplish this the reducible representation formed by the group operations on the ψ_i before linear combinations were taken must be obtained. This is done in the same manner as for the directed valence method except the wave functions of the attached atoms are considered rather than those of the central atom. The reducible representation is then broken down into its irreducible representations by the method described in the section on group theory. The irreducible representations for which the orbitals of the central atom form bases may also be obtained in the manner previously discussed. Only the central orbitals which form bases for the irreducible representations contained in the reducible representation of the ψ_i functions can be used to form bonds with the attached atoms. The central orbitals which form bases for other irreducible representations cannot take part in the bonding and consequently are called nonbonding.

The values for the coefficients a_i have been tabulated by Van Vleck and Sherman[15] for various structures.

The preceding discussion of the molecular orbital method dealt with the problem of a central atom surrounded

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[15] J.H. Van Vleck and Albert Sherman, Rev. Mod. Phys. 7, 167, 1935.

by several attached atoms arranged in a certain symmetrical manner. A portion of this particular problem also requires applying the molecular orbital method to a symmetrical structure with no central atom. The treatment of this type of structure varies somewhat from that above. This will be discussed later.

In this discussion the emphasis has been placed on the difference between these two methods. It should be pointed out, however, that if all of the possible refinements to these two methods are considered; they both will yield essentially the same molecular wave function. They differ only in taking a different wave function as the starting point of a pertubation calculation. However, one method may be preferred to the other depending on the type of problem. The directed valence method seems to apply more naturally when dealing with the problem of bonding in a molecule since bonds are usually considered as being between two atoms rather than extending throughout the entire molecule. On the other hand, when dealing with properties of the molecule as a whole, such as the energy levels, the molecular orbital method seems more applicable. In many problems the directed valence method probably lends itself better to obtaining quantitative results, although this is not always true. On the other hand, the molecular orbital method is often used to discuss the properties of a molecule in a qualitative manner.

Only a general discussion of the two types of bonding has been given. For a more detailed discussion of either the directed valence[16,17,18,19,20,21] or molecular orbital[16,17,22,23] method it will be necessary to refer to various texts and articles on the subject.

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[16]Eyring, Walter, and Kimball, op. cit.

[17]Samuel Glasstone, Theoretical Chemistry, D. Van Nostrand Company, Inc.: Princeton, 1944.

[18]Ralph Hultgran, Phys. Rev. 40, 891, 1932.

[19]Linus Pauling, The Nature of the Chemical Bond, 3rd. ed., Cornell University Press: New York, 1960.

[20]Linus Pauling, J. Am. Chem. Soc. 54, 988, 3570, 1932.

[21]G.E. Kimball, J. Chem. Phys. 8, 188, 1940.

[22]Robert S. Mulliken, Phys. Rev. 41, 49, 1932.

[23]J.H. Van Vleck, J. Chem. Phys. 3, 803, 1935.

CENTRAL ATOM BONDING IN THE CUBOCTAHEDRAL STRUCTURE

The discussion of group theory and bonding given in the previous sections will be made use of in explaining the bonding in the cuboctahedral structure. This is a cubic close-packed structure[23] where 12 atoms are arranged about a central atom. These 12 atoms are located at the vertices of a cuboctahedron. Many substances have this structure.[24] It is common in ionic structures and is possible in covalent ones.

Macek and Duffey[25] have considered the regular-icosahedral AB_{12}. This section considers the corresponding cuboctahedron.

The cuboctahedron is oriented as in Figure 1, with the ligands (attached atoms) numbered as shown. A bond between the central atom and the ith attached atom is called bond orbital ψ_i. These functions are listed in Table I.

The symmetry operations which leave the cuboctahedron unchanged form the O_h group. The operations of this group are as follows: (1) The identity operation. (2) Four C_3

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[23] A.F. Wells, Solid State Physics, vol. 7, 426, Academic Press, Inc.: New York, 1958.

[24] Linus Pauling, The Nature of the Chemical Bond, 3rd. ed., Cornell University Press: New York, 1960.

[25] Joseph H. Macek and George H. Duffey, J. Chem. Phys. 34, 288, 1961.

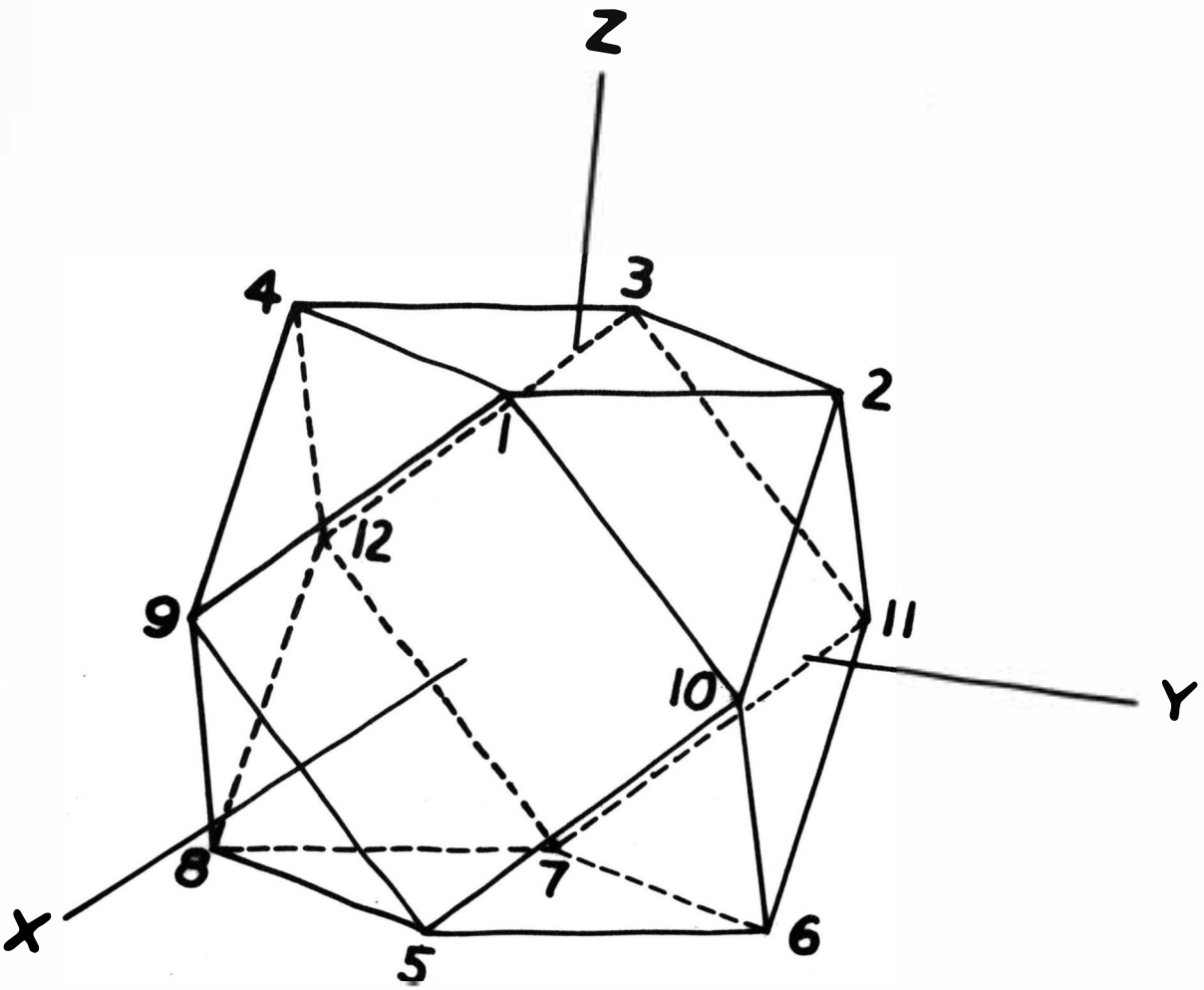

Figure 1. Orientation of Cuboctahedron

TABLE I. COEFFICIENTS OF ATOMIC ORBITALS IN CUBOCTAHEDRAL BOND ORBITAL FUNCTIONS.

	s	p_x	p_y	p_z	$d_{3z^2-r^2}$	$d_{x^2-y^2}$	d_{xz}	d_{yz}	d_{xy}	$f_{\epsilon 1}$	$f_{\epsilon 2}$	$f_{\epsilon 3}$	$f_{\epsilon 1}$	$f_{\epsilon 2}$	$f_{\epsilon 3}$
ψ_1	$\frac{1}{\sqrt{12}}$	$\frac{1}{\sqrt{8}}\cos\alpha$	0	$\frac{1}{\sqrt{8}}\cos\alpha$	$\frac{1}{\sqrt{24}}$	$\frac{1}{\sqrt{8}}$	$\frac{1}{2}$	0	0	$\frac{-1}{\sqrt{8}}\sin\alpha$	$\frac{-1}{\sqrt{8}}\sin\alpha$	0	$\frac{1}{\sqrt{8}}$	$\frac{1}{\sqrt{8}}$	0
ψ_2	$\frac{1}{\sqrt{12}}$	0	$\frac{1}{\sqrt{8}}\cos\alpha$	$\frac{1}{\sqrt{8}}\cos\alpha$	$\frac{1}{\sqrt{24}}$	$\frac{-1}{\sqrt{8}}$	0	$\frac{1}{2}$	0	$\frac{-1}{\sqrt{8}}\sin\alpha$	0	$\frac{-1}{\sqrt{8}}\sin\alpha$	$\frac{-1}{\sqrt{8}}$	0	$\frac{1}{\sqrt{8}}$
ψ_3	$\frac{1}{\sqrt{12}}$	$\frac{-1}{\sqrt{8}}\cos\alpha$	0	$\frac{1}{\sqrt{8}}\cos\alpha$	$\frac{1}{\sqrt{24}}$	$\frac{1}{\sqrt{8}}$	$-\frac{1}{2}$	0	0	$\frac{-1}{\sqrt{8}}\sin\alpha$	$\frac{1}{\sqrt{8}}\sin\alpha$	0	$\frac{1}{\sqrt{8}}$	$\frac{-1}{\sqrt{8}}$	0
ψ_4	$\frac{1}{\sqrt{12}}$	0	$\frac{-1}{\sqrt{8}}\cos\alpha$	$\frac{1}{\sqrt{8}}\cos\alpha$	$\frac{1}{\sqrt{24}}$	$\frac{-1}{\sqrt{8}}$	0	$-\frac{1}{2}$	0	$\frac{-1}{\sqrt{8}}\sin\alpha$	0	$\frac{1}{\sqrt{8}}\sin\alpha$	$\frac{-1}{\sqrt{8}}$	0	$\frac{-1}{\sqrt{8}}$
ψ_5	$\frac{1}{\sqrt{12}}$	$\frac{1}{\sqrt{8}}\cos\alpha$	0	$\frac{-1}{\sqrt{8}}\cos\alpha$	$\frac{1}{\sqrt{24}}$	$\frac{1}{\sqrt{8}}$	$-\frac{1}{2}$	0	0	$\frac{1}{\sqrt{8}}\sin\alpha$	$\frac{-1}{\sqrt{8}}\sin\alpha$	0	$\frac{-1}{\sqrt{8}}$	$\frac{1}{\sqrt{8}}$	0
ψ_6	$\frac{1}{\sqrt{12}}$	0	$\frac{1}{\sqrt{8}}\cos\alpha$	$\frac{-1}{\sqrt{8}}\cos\alpha$	$\frac{1}{\sqrt{24}}$	$\frac{-1}{\sqrt{8}}$	0	$-\frac{1}{2}$	0	$\frac{1}{\sqrt{8}}\sin\alpha$	0	$\frac{-1}{\sqrt{8}}\sin\alpha$	$\frac{1}{\sqrt{8}}$	0	$\frac{1}{\sqrt{8}}$
ψ_7	$\frac{1}{\sqrt{12}}$	$\frac{-1}{\sqrt{8}}\cos\alpha$	0	$\frac{-1}{\sqrt{8}}\cos\alpha$	$\frac{1}{\sqrt{24}}$	$\frac{1}{\sqrt{8}}$	$\frac{1}{2}$	0	0	$\frac{1}{\sqrt{8}}\sin\alpha$	$\frac{1}{\sqrt{8}}\sin\alpha$	0	$\frac{-1}{\sqrt{8}}$	$\frac{-1}{\sqrt{8}}$	0
ψ_8	$\frac{1}{\sqrt{12}}$	0	$\frac{-1}{\sqrt{8}}\cos\alpha$	$\frac{-1}{\sqrt{8}}\cos\alpha$	$\frac{1}{\sqrt{24}}$	$\frac{-1}{\sqrt{8}}$	0	$\frac{1}{2}$	0	$\frac{1}{\sqrt{8}}\sin\alpha$	0	$\frac{1}{\sqrt{8}}\sin\alpha$	$\frac{1}{\sqrt{8}}$	0	$\frac{-1}{\sqrt{8}}$
ψ_9	$\frac{1}{\sqrt{12}}$	$\frac{1}{\sqrt{8}}\cos\alpha$	$\frac{-1}{\sqrt{8}}\cos\alpha$	0	$\frac{-1}{\sqrt{6}}$	0	0	0	$-\frac{1}{2}$	0	$\frac{-1}{\sqrt{8}}\sin\alpha$	$\frac{1}{\sqrt{8}}\sin\alpha$	0	$\frac{-1}{\sqrt{8}}$	$\frac{1}{\sqrt{8}}$
ψ_{10}	$\frac{1}{\sqrt{12}}$	$\frac{1}{\sqrt{8}}\cos\alpha$	$\frac{1}{\sqrt{8}}\cos\alpha$	0	$\frac{-1}{\sqrt{6}}$	0	0	0	$\frac{1}{2}$	0	$\frac{-1}{\sqrt{8}}\sin\alpha$	$\frac{-1}{\sqrt{8}}\sin\alpha$	0	$\frac{-1}{\sqrt{8}}$	$\frac{-1}{\sqrt{8}}$
ψ_{11}	$\frac{1}{\sqrt{12}}$	$\frac{-1}{\sqrt{8}}\cos\alpha$	$\frac{1}{\sqrt{8}}\cos\alpha$	0	$\frac{-1}{\sqrt{6}}$	0	0	0	$-\frac{1}{2}$	0	$\frac{1}{\sqrt{8}}\sin\alpha$	$\frac{-1}{\sqrt{8}}\sin\alpha$	0	$\frac{1}{\sqrt{8}}$	$\frac{-1}{\sqrt{8}}$
ψ_{12}	$\frac{1}{\sqrt{12}}$	$\frac{-1}{\sqrt{8}}\cos\alpha$	$\frac{-1}{\sqrt{8}}\cos\alpha$	0	$\frac{-1}{\sqrt{6}}$	0	0	0	$\frac{1}{2}$	0	$\frac{1}{\sqrt{8}}\sin\alpha$	$\frac{1}{\sqrt{8}}\sin\alpha$	0	$\frac{1}{\sqrt{8}}$	$\frac{1}{\sqrt{8}}$

and four C_3^2 operations in the C_3 class, which are counterclockwise rotations of 120 degrees and 240 degrees, respectively, about the four axes through the center of opposite triangles. (3) Six C_2 operations in the C_2 class, which are counterclockwise rotations of 180 degrees about the six axes through opposite vertices. (4) Three C_4 and three C_4^3 operations in the C_4 class, which are counterclockwise rotations of 90 degrees and 270 degrees, respectively, about the three axes through the centers of opposite squares. (5) Three C_4^2 operations in the C_4^2 class, which are counterclockwise rotations of 180 degrees about the three axes through the center of opposite squares. (6) One S_2 or inversion operation in the S_2 class, which is an inversion of all points through the center of symmetry. (7) Three S_4 and three S_4^3 operations in the S_4 class, which are counterclockwise rotations of 90 degrees and 270 degrees, respectively, about the same axes as for the C_4 class, followed by an inversion through the center of symmetry. (8) Four S_6 and four S_6^5 operations in the S_6 class, which are counterclockwise rotations of 60 degrees and 300 degrees, respectively, about the same axes as for class C_3, followed by an inversion through the center of symmetry. (9) Three σ_h operations in the σ_h class, which are reflections in the three planes perpendicular to the three C_4 axes. (10) Six σ_d operations in the σ_d class, which are reflections in the six planes, each of which contains one major axis (the C_4 axes)

and only one of the C_2 axes.

The character table for the O_h group is taken from Herzberg[26] and is shown in Table II. There are several things besides the irreducible representations and their characters shown in the character table. In the left hand column the orbitals of the central atoms are listed on the same line as the irreducible representations for which they form a basis. On the first line below the characters for the F_{2u} irreducible representation, the characters of the reducible σ representation are entered. The $\underline{\sigma}$ bonds are those which are formed by overlapping of a hybrid central atom orbital with an orbital from the attached atom, where both orbitals are symmetric about the line joining the two atoms. The characters for the π reducible representation are listed next. A $\underline{\pi}$ bond is a bond between the central orbital and ligand which is formed by the overlapping of two parallel orbitals which are at right angles to the σ bond. This type of bonding will be discussed later. The σ_x' and σ_y' reducible representations are also listed and will be explained when the bonding between the attached atoms is treated.

The symbols in the second column under O_h indicate the particular irreducible representation. The A's indcate one-dimensional, the E's two-dimensional, and the F's

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[26] Gerhard Herzberg, op. cit.

TABLE II. CHARACTER TABLE OF O_h GROUP.

Basis orbitals	Representation	E	$8C_3$	$6C_2$	$6C_4$	$3C_4^2$	S_2	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
s	A_{1g}	1	1	1	1	1	1	1	1	1	1
	A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1
	A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1
f_β	A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1
$d_{\gamma 1}, d_{\gamma 2}$	E_g	2	-1	0	0	2	2	0	-1	2	0
	E_u	2	-1	0	0	2	-2	0	1	-2	0
	F_{1g}	3	0	-1	1	-1	3	1	0	-1	-1
p_x, p_y, p_z $f_{\delta 1}, f_{\delta 2}, f_{\delta 3}$	F_{1u}	3	0	-1	1	-1	-3	-1	0	1	1
$d_{\epsilon 1}, d_{\epsilon 2}, d_{\epsilon 3}$	F_{2g}	3	0	1	-1	-1	3	-1	0	-1	1
$f_{\epsilon 1}, f_{\epsilon 2}, f_{\epsilon 3}$	F_{2u}	3	0	1	-1	-1	-3	1	0	1	-1
	σ	12	0	2	0	0	0	0	0	4	2
	π	24	0	-4	0	0	0	0	0	0	0
	σ'_x	12	0	-2	0	0	0	0	0	-4	2
	σ'_y	12	0	-2	0	0	0	0	0	4	-2

three-dimensional representations. The g(gerade) and the u(ungerade) refer to representations which are symmetric and antisymmetric, respectively, with respect to inversion through the center of symmetry. If the representation is symmetric, the character of the S_2 operation will be positive; if it is antisymmetric, the sign will be negative.

The directed valence method will be employed in determining the bonding functions. The nonradial portion of the s, p, d, and hydrogen-like orbitals of the central atom A which form bases for the irreducible representations are listed by Eisenstein.[27] These orbitals are normalized to 4π. It will be assumed that the radial portions of all of the orbitals are approximately the same. These functions can be written as:

$$
\begin{aligned}
&\Psi(s) = \Psi = 1 \\
&\Psi(p_x) = \Psi_x = \sqrt{3}\sin\theta\cos\phi \\
&\Psi(p_y) = \Psi_y = \sqrt{3}\sin\theta\sin\phi \\
&\Psi(p_z) = \Psi_z = \sqrt{3}\cos\theta \\
&\Psi(d\gamma 1) = \Psi_{3z^2-r^2} = \frac{\sqrt{5}}{2}(3\cos^2\theta - 1) \\
&\Psi(d\gamma 2) = \Psi_{x^2-y^2} = \frac{\sqrt{15}}{2}\sin^2\theta\cos 2\phi \\
&\Psi(d\epsilon 1) = \Psi_{xy} = \frac{\sqrt{15}}{2}\sin^2\theta\sin 2\phi \\
&\Psi(d\epsilon 2) = \Psi_{xz} = \sqrt{15}\sin\theta\cos\theta\cos\phi \\
&\Psi(d\epsilon 3) = \Psi_{yz} = \sqrt{15}\sin\theta\cos\theta\sin\phi \\
&\Psi(f_\beta) = \Psi_{xyz} = \frac{\sqrt{105}}{2}\sin^2\theta\cos\theta\sin 2\phi
\end{aligned}
\qquad (17)
$$

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[27] J.C. Eisenstein, J. Chem. Phys. 25, 142, 1956.

$$\psi(f_{\delta 1}) = \psi_{z(5z^2-3r^2)} = \frac{\sqrt{7}}{2}(5\cos^3\theta - 3\cos\theta)$$

$$\psi(f_{\delta 2}) = \psi_{x(5x^2-3r^2)} = \frac{\sqrt{7}}{2}\sin\theta\cos\phi(5\sin^2\theta\cos^2\phi - 3)$$

$$\psi(f_{\delta 3}) = \psi_{y(5y^2-3r^2)} = \frac{\sqrt{7}}{2}\sin\theta\sin\phi(5\sin^2\theta\sin^2\phi - 3)$$

$$\psi(f_{\epsilon 1}) = \psi_{(x^2-y^2)z} = \frac{\sqrt{105}}{2}\sin^2\theta\cos\theta\cos 2\phi$$

$$\psi(f_{\epsilon 2}) = \psi_{(z^2-y^2)x} = \frac{\sqrt{105}}{2}\sin\theta\cos\phi(\cos^2\theta - \sin^2\theta\sin^2\phi)$$

$$\psi(f_{\epsilon 3}) = \psi_{(z^2-x^2)y} = \frac{\sqrt{105}}{2}\sin\theta\sin\phi(\cos^2\theta - \sin^2\theta\cos^2\phi)$$

In the first expression for each wave function, the letters indicate the particular atomic orbital and Greek letter subscripts indicate which orbitals transform in the same manner under the operations of the group. All orbitals which have the same Greek letter subscripts transform in the same manner and form a degenerate set which is the basis for some irreducible representation. The fact that some of the d and f orbitals form bases for different irreducible representations indicates that these sets have different energies. This is due to the splitting of levels which was mentioned in the section on group theory.

In the second notation for the wave functions, the polynomial subscript describes the nonradial variation of the orbital. The nodal surfaces for each orbital can be obtained by setting the subscript equal to zero. For instance, the f_{xyz} orbital has nodal surfaces at x=0, y=0, and z=0.

To find which functions form a basis for each irreducible representation, one has to operate on all of the orbitals with an operator from each class. Any set of or-

bitals which transform into linear combinations of each other will form a basis for an irreducible representation. Actually, it will only be necessary to determine how each polynomial subscript transforms under the operations since the orbital will transform in the same manner. To determine the particular representation for which the functions form a basis requires that the matrices representing the transformation for each class of operations be constructed. The functions will form a basis for the irreducible representation which has the same characters for corresponding classes. In this manner it is possible to determine for which irreducible representations the orbitals form bases.

The next step is to determine the character of the reducible representation. This is done by finding how many of the σ bonds are transformed into themselves under an operation from each class. This will indicate how many ones appear on the diagonals of the permutation matrices which form a representation of the group. The total number will be equal to the character of the matrix.

The reducible representation can be broken down into its irreducible components by making use of equations (7) and (8). This will yield the relation

$$\sigma = A_{1g} + E_g + F_{1u} + F_{2g} + F_{2u} \qquad (18)$$

This indicates that only the functions which form bases for the irreducible representations above can be used in forming the σ bonds. It can be seen from the character table

that the f_β orbital is the only one which cannot take part in the σ bonding since it forms a basis for the A_{2u} irreducible representation which does not appear in the σ representation. This is to be expected since all of the bond orbitals lie in one of the three nodal surfaces of f_β.

It will be noted that both sets p_x, p_y, p_z and $f_{\delta 1}$, $f_{\delta 2}$, $f_{\delta 3}$ form bases for the F_{1u} irreducible representation. This indicates that either the p or the f_δ orbitals could be used in the bonding functions. However, the most general results will be obtained by using a linear combination of both sets. It is most convenient to pair each p orbital with the f_δ orbital which transforms in the same manner under <u>each</u> operation of the group. Of course, the set of p orbitals and the set of f_δ orbitals must transform in the same manner under each <u>class</u> of operations. However, each orbital in these sets may, and in general does, transform differently under any particular operation.

The manner in which these orbitals will pair can be determined by considering the orientation of their nodal surfaces. The p_z and $f_{\delta 1}$ orbitals both have nodal surfaces at z=0. This indicates that neither function will contribute anything to bonds 9, 10, 11, and 12 since they lie in this plane. The other eight bonds are located symmetrically with respect to this plane so that p_z will contribute an equal amount to each of these. The $f_{\delta 1}$ orbital also has two other nodal surfaces. They are cones with apex at

the origin and symmetrical about the positive and negative z-axis. Consequently, the remaining eight bonds are also located symmetrically with respect to these surfaces, and the $f_{\delta 1}$ orbital will contribute equally to each. From the argument above, it can be concluded that if either the p orbitals or the f_{δ} orbitals were to be used alone, rather than a linear combination, then the coefficient of the p_z and $f_{\delta 1}$ terms would be the same for all eight bonds.

Since a linear combination of the p and $f_{\delta 1}$ orbitals is being used, it will be necessary to relate p_z and $f_{\delta 1}$ by a parameter; and the value of the parameter which will give the strongest bonding will be determined. Since all the original orbitals are normalized to 4π, it would be desirable to have the linear combinations normalized to the same constant. This requires that the sum of the squares of the parametric coefficients of the p_z and $f_{\delta 1}$ terms equal one in the linear combination. The coefficients $\cos\alpha$ (for p_z) and $\sin\alpha$ (for $f_{\delta 1}$) satisfy this condition.

It can be shown in the same manner that p_x and $f_{\delta 2}$ and p_y and $f_{\delta 3}$ are similarly related.

All the necessary information is now available for determining the form of the twelve bond functions. These bonds are shown in Table I.

Since the s orbital is spherically symmetric about the central atom, it will contribute equally to all the bonds so that its coefficient in each bond will be $\frac{1}{\sqrt{12}}$.

The choice of the coefficients is based on the fact that the rows of coefficients are orthogonal and normalized to one. The reason for this is that it is desirable to construct 12 linear combinations of the orthonormal atomic orbitals which will be orthogonal and normalized to 4π. Since the atomic orbitals are normalized to 4π, the condition that the linear combinations will be normalized to the same constant is that the sum of the squares of the coefficients be equal to one. If these orthonormal conditions are satisfied for the rows of coefficients, it follows that they will be satisfied for the columns also. This indicates that the sum of the squares of the contributions of each atomic orbital must equal one.

In considering the s orbital, the coefficients must be equal since it contributes equally to all bonds. They must also satisfy the condition that the sum of the squares is equal to one. It follows that the coefficients are all necessarily $\frac{1}{\sqrt{12}}$ as stated above. It can be seen from this argument that the contribution of a particular orbital to a bonding function is equal to the square of its coefficient in the expression for that function.

The fact that p_z and $f_{\delta 1}$ contribute equally to bonds 1-8 and not at all to bonds 9-12 has already been discussed. Consequently, the coefficient for p_z will be $\frac{\cos\alpha}{\sqrt{8}}$, and for $f_{\delta 1}$ it will be $\frac{\sin\alpha}{\sqrt{8}}$ for bonds 1-8, and zero for bonds 9-12.

Similar arguments can be employed to show that p_x

and $f_{\delta 2}$ make no contribution to bonds 2, 4, 6, and 8, and equal contributions to the remaining eight bonds. Similarly, p_y and $f_{\delta 3}$ make no contribution to bonds 1, 3, 5, and 7, but contribute equally to the other eight.

The signs of all of the coefficients can be determined by plugging the appropriate angles into the expressions for the orbitals and determining the sign for each bond. If the exact angles were not known, it would be necessary to make an assumption about the signs and then check the results. One may determine the appropriate signs by considering the position of the bonds relative to the nodal surfaces.

Next consider the contributions from the d_γ orbitals. The $d_{\gamma 2}$ orbital has nodal surfaces at x=y. Since bonds 9-12 lie in these nodal planes, $d_{\gamma 2}$ will not contribute to them. Bonds 1-8 are located symmetrically with respect to these surfaces so that the contribution to each of these bonds will be the same. Since all the $d_{\gamma 2}$ orbitals are used in bonding, the sum of the squares of the coefficients for each orbital will be one. Consequently, the coefficient of the $d_{\gamma 2}$ orbital in bonds 1-8 is $\frac{1}{\sqrt{8}}$ and in bonds 9-12 is zero. Since $d_{\gamma 1}$ and $d_{\gamma 2}$ form a basis for an irreducible representation, the total contribution of the two orbitals(not each individually) must be the same for each bond. There are 12 bonds and a total of two orbitals to share among them so that the total contribution of the

two orbitals in each bond is $\frac{2}{12}$. This means that the contribution of $d_{\gamma 1}$ to bonds 9-12 must be the total $\frac{2}{12}$ so that each coefficient will be $\frac{1}{\sqrt{6}}$. This then requires that the $d_{\gamma 1}$ coefficients in bonds 1-8 must be $\frac{1}{\sqrt{24}}$. Since $d_{\gamma 1}$ contributes different amounts to bonds 1-8 and bonds 9-12, it indicates that these two sets of bonds must not be located symmetrically with respect to the nodal surfaces. This can be verified from the figure. It can be seen that bonds 9-12 are located symmetrically with respect to the nodal surfaces which are cones with apexes at the origin and symmetric about the positive z-axis and one about the negative z-axis. Bonds 1-8 are also located symmetrically about these surfaces, but they are closer to the surface than bonds 9-12 so it would be expected that $d_{\gamma 1}$ would contribute less to them. This is verified by the previous argument.

The d_{ϵ} orbitals will be considered next. The $d_{\epsilon 1}$ orbital has nodal surfaces at x=0 and y=0. It can be seen from Figure 1 that x=0 passes through bonds 2, 4, 6, and 8; and y=0 passes through bonds 1, 3, 5, and 7 so that $d_{\epsilon 1}$ will not contribute anything to these bonds. Bonds 9-12 are arranged symmetrically with respect to these surfaces; and, consequently, $d_{\epsilon 1}$ will contribute equally to them. The sum of the squares of the coefficients must be one so each coefficient for bonds 9-12 will be $\frac{1}{2}$ and the remainder zero.

It can be shown that $d_{\epsilon 2}$ contributes to 1, 3, 5, and 7 and $d_{\epsilon 3}$ to bonds 2, 4, 6, and 8 in the same manner by using similar arguments.

Only the f_{ϵ} orbitals are left since it was determined that f_{β} does not contribute to the bonds. The $f_{\epsilon 1}$ orbital has nodal surfaces which are cones with apex at the origin and symmetric with respect to the z-axis and a plane at z=0. The plane passes through bonds 9-12 so $f_{\epsilon 1}$ will contribute nothing to these bonds. The rest of the bonds are located symmetrically about the surfaces so that $f_{\epsilon 1}$ will contribute equally to all of them. Therefore, the coefficients of the bonds 1-8 are $\frac{1}{\sqrt{8}}$ and those for bonds 9-12 are zero.

The argument proceeds in the same manner for the $f_{\epsilon 2}$ and $f_{\epsilon 3}$ orbitals. The orbital $f_{\epsilon 2}$ contributes nothing to bonds 2, 4, 6, and 8 since one of its nodal surfaces passes through these bonds; and it contributes equally to the others. Likewise, $f_{\epsilon 3}$ contributes nothing to bonds 1, 3, 5, and 7 and equally to the others. It can also be seen that the total contribution of the f_{ϵ} orbitals is the same for each bond. This completes Table I.

The bonds can be checked in several ways. As mentioned above, the total contribution of the orbitals forming a basis for an irreducible representation should be the same for each bond. Also the total contribution of a particular orbital to all of the bonds must be one except

when two sets form a basis for the same irreducible representation. Since the bonds are equivalent, by definition it should be possible to rotate any bond into any other one by substituting the proper values for θ and ϕ. Normalization and orthogonality conditions were imposed on the 12 linear combinations when they were constructed. Consequently, the coefficients of these functions should be normalized to one and orthogonal to each other. These conditions are all satisfied by the 12 bonding functions in Table I.

The energy of a covalent bond is essentially the energy of resonance of two electrons between two atoms. This resonance energy will increase with the increase in the overlapping of the two orbitals. Consequently, the more the hybrid orbital of the central atom extends in the direction of the ligand; the stronger the bond. Since the radial portion of all the orbitals which are being used in the bonding are assumed to be nearly equal, the numberical value of the angular part in a particular direction will indicate the extension of the orbital in this direction. Pauling[28] calls this the bond strength S. It can be obtained by putting in the appropriate values for the angles.

According to Pauling and Glasstone[29], the bond en-

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[28]Linus Pauling, The Nature of the Chemical Bond, 3rd. ed., Cornell University Press: New York, 1960.

[29]Glasstone, op. cit.

ergy of a covalent bond between the central atom and an attached atom is proportional to the strength of the central atom bonding orbital. The energy of this bond is also proportional to the strength of the attached atom bonding orbital.

It is now necessary to determine the amount of p and f_δ orbitals in the bond orbitals which will give the largest value of the bond orbital in the direction of the ligand and, consequently, the maximum bond strength. This is done by differentiating ψ(any one of the 12) with respect to α, equating this to zero, and solving for α.

The over-all composition of the bond orbitals is $sp^{3n}d^5f^{6-3n}$ where

$$n = \cos^2\alpha \qquad (19)$$

If none of the f_δ orbitals are used in the bonds (n=1), then S is equal to 3.860. This is considerably less than 3.921 which is the strength of the icosahedral orbital with the same composition. It would be expected that the overlap of the central atoms with the ligand orbitals would be greater in the icosahedral structure. However, S increases to a maximum of 3.921 when the amount of f is increased to 3.380. Since this is the same as the maximum for the icosahedral, the cuboctahedral structure would not be favored unless the f orbitals have low energies. The manner in which S varies with n is shown in Table III.

Since the ligands are closer together in the cub-

TABLE III. PROPERTIES OF CUBOCTAHEDRAL BOND ORBITALS.[a]

n	cos∝	S
0.0000	0.0000	3.325
0.2000	0.4472	3.677
0.4000	0.6325	3.798
0.6000	0.7746	3.874
0.8000	0.8944	3.917
0.8735	0.9346	3.921
1.0000	1.0000	3.860

[a]The orbitals are of type $\underline{sp}^{3n}\underline{d}^{5}\underline{f}^{6-3n}$

octahedron, if the interactions between them are such that they attract, this structure will be favored.

The concept of π bonding was mentioned previously. They were described as bonds formed by the overlapping of a central bond orbital and a ligand orbital which are at right angles to the σ bonds.

The reducible representation for π bonds is shown in Table II. This representation is found in the same manner as for the σ bonds except that the p orbitals of the attached atom which are perpendicular to the σ bonds are considered rather than the hybrid central orbitals. This reducible representation breaks down into irreducible rep-

resentations

$$A_{2g} + A_{2u} + E_g + E_u + 2F_{1g} + 2F_{1u} + F_{2g} + F_{2u} \qquad (20)$$

Only central bond orbitals which form bases for these irreducible representations can take part in the π bonding. It can be seen from Table II that no bases functions for A_{2g}, E_u, or F_{1g} are available among the s, p, d, and f orbitals. It would be necessary that higher orbitals be available if these types of π bonds were to be formed. All of the s, p, d, and f orbitals of the E_g, F_{2g}, and F_{2u} representations are used in the σ bonds so that these kinds of π bonds are not expected. Three of the six orbitals p_x, p_y, p_z, $f_{\delta 1}$, $f_{\delta 2}$, and $f_{\delta 3}$ which form bases for F_{1u} are used in the σ bonds. The rest are available for π bonding. Since F_{1u} appears twice in the reducible representation, three higher orbitals would be necessary to complete all bonds of this type. These are called weak π bonds because some of the orbitals needed to complete these bonds are used in the σ bonds. The A_{2u} representation is spanned by f . Since this orbital is not used in σ bonds, it is available for π bonding. This π bond is strong.

MOLECULAR ORBITAL BONDING IN THE CUBOCTAHEDRAL STRUCTURE

There is another problem involving the cuboctahedral structure which is of interest. This concerns the bonding between 12 atoms arranged at the vertices of a cuboctahedron with no central atom. Lipscomb and Britton[30] consider this arrangement; but the method they used involves making some assumptions, which will be discussed later, about the interactions of the atoms with their various neighbors. They have evidently used the variation method[31], which requires solving a secular determinant. The approximations mentioned above were necessary to simplify this determinant.

The energy levels can be found, however, without solving a secular determinant. This can be accomplished by making use of group theory to find the necessary wave functions rather than using the variation method.

The LCAO molecular orbital method described in the section on bonding will be used to determine these wave functions. However, since there is no central atom involved, the molecular orbitals will be constructed only from the atomic orbitals of the attached atoms.

The mathematical expression for the atomic orbitals

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[30] William N. Lipscomb and Dayle Britton, J. Chem. Phys. 33, 275, 1960.

[31] Glasstone, Laidler, and Eyring, The Theory of Rate Processes, pp. 62-66, McGraw Hill Book Company: New York, 1941.

will not be considered. The energy levels will be found in terms of integrals involving these functions and the Hamiltonian operator. No attempt will be made to evaluate these integrals.

The same set of atomic orbitals that Lipscomb and Britton considered will be used here. They are the spherically symmetric s orbitals, the p_x orbitals on each atom tangential to the sphere circumscribing the cuboctahedron and pointing toward the centers of the triangular faces, the p_y orbitals tangential to the sphere and pointing toward the centers of the squares, and the p_z orbitals directed radially outward. The s and p_z orbitals can be combined to form two sets of orbitals; one set pointing radially outward to form external bonds, and one set pointing toward the center of the cuboctahedron. The external sp_z orbitals will not be considered; only those involved in the bonding within the structure.

The reducible representations formed by operating on each of the three sets, sp_z, p_x, and p_y are shown in Table II. Since the sp_z orbitals point toward the center of the structure they will form the same reducible representation as the σ bonds of the central atom. The reducible representation formed by the p_x orbitals is represented by σ'_x, and that formed by the p_y orbitals as σ'_y. The primes are used to distinguish these bonds from the σ bonds previously described. Since the p_x and p_y orbitals are tangential to

the sphere, the overlapping orbitals will not be symmetric about a line joining the two atoms as in the central atom bonding, but will be symmetric about lines which meet at an angle. The same is true of the sp_z orbitals pointing toward the center of the sphere. There are exceptions to this. The sp_z orbitals form σ bonds, and the p_x and p_y orbitals form π bonds when the two atoms considered are on opposite vertices of the structure. The p_x orbitals also form $\pi\pi$ bonds when the two atoms considered are located on opposite corners of any of the square faces.

The method which will be used to determine the molecular orbitals and the corresponding energy levels is essentially that of Eyring, Walter, and Kimball.[33]

The molecular orbitals will be formed from linear combinations of atomic orbitals. Three sets of molecular orbitals will be considered. These are the sets formed by linear combinations of sp_z orbitals, linear combinations of p_x orbitals, and linear combinations of p_y orbitals.

Since the molecular orbitals are formed from linear combinations of the atomic orbitals, the atomic orbitals can also be written as linear combinations of the molecular orbitals. These linear combinations can be written

$$\psi' = \sum_i \sum_{k=1}^{s_i} \sum_{m=1}^{d_i} C^i_{km} \psi^i_{km} \qquad (21)$$

In this expression ψ' represents the atomic orbitals, and

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[33] Eyring, Walter, and Kimball, op. cit.

ψ^i_{km} represents the molecular orbitals belonging to the ith irreducible representation of dimension d_i with the eigenvalue E^i_k. The summation over m indicates that the number of independent functions which form a basis for an irreducible representation is equal to the dimension of the representation. This has been discussed previously. If there are s_i sets of functions forming a bases for the ith irreducible representation, then the total number of functions corresponding to this representation is $d_i \times s_i$. This accounts for the summation over k. The summation over all i irreducible representations will yield the total number of independent molecular orbitals forming bases for these representations. It follows that the total number of independent molecular orbitals is

$$\sum_i s_i \times d_i \tag{22}$$

If R is any operation of the group, then by equation (12)

$$R\psi' = \sum_i \sum_{k=1}^{s_i} \sum_{m=1}^{d_i} C^i_{km} \sum_{n=1}^{d_i} \psi^i_{kn} A^i_{nm} \tag{23}$$

If equation (23) is multiplied by

$$\chi^j(R) = \sum_{t=1}^{d_j} A^j_{tt} \tag{24}$$

which is the character corresponding to operation R and irreducible representation j; and summed over all R, it becomes

$$\sum_R \chi^j(R) R\psi' = \sum_i \sum_{k=1}^{s_i} \sum_{m=1}^{d_i} C^i_{km} \sum_{n=1}^{d_i} \sum_{t=1}^{d_j} \sum_R \psi^i_{kn} A^j_{tt} A^i_{nm} \tag{25}$$

Equation (2) will reduce this to

$$\sum_R \chi^j(R) R\psi' = \sum_i \sum_{k=1}^{s_i} \sum_{m=1}^{d_j} C^j_{km} \sum_{n=1}^{d_j} \sum_{t=1}^{d_j} \psi^j_{kn} \frac{g}{d_j} \delta_{tn} \delta_{tm} \tag{26}$$

If only the functions which form a basis for the jth irreducible representation are desired, the first summation over i can be omitted; and this yields

$$\sum_R \chi^j(R) R\psi' = \sum_{k=1}^{s_j} \sum_{m=1}^{d_j} \frac{g}{d_j} C^j_{kt} \psi^j_{kt} \qquad (27)$$

The last three summations in equation (26) are all combined into one.

In order to find all of the necessary linear combinations of the ψ' functions, it will be necessary to determine $\Sigma \chi^j(R) R\psi'$ for each ψ'. The results of these operations are given in Table III. For the sp_z, p_x, and p_y orbitals ψ' is represented by r_1, t_1, and s_1, respectively. The capital letters represent the operations as described previously. The pairs of small letters and numbers indicate the axis of rotation for rotation operations, and the axes contained in the planes of reflection for the reflection operations. The planes of reflections for the operations are represented by two axis indicating that the plane must contain these axes. The axes run through the vertices represented by the numbers, or through the centers of opposite faces represented by the letters.

In Figure 1, a is in center of triangular face bounded by vertices 6, 7, and 11; b by 5, 6, and 10; c by 1, 4, and 9; d by 3, 4, and 12; e by 2, 3, and 11; f by 1, 2, and 10; g by 5, 8, and 9; and h by 7, 8, and 12. Also i is in the center of the square bounded by vertices 5, 6, 7, and 8; j by 3, 7, 11, and 12; k by 1, 2, 3, and 4; l by 1, 5, 9,

TABLE III. APPLICATION OF GROUP OPERATIONS TO sp_3, p_{3x} AND p_y ORBITALS.

	I	σ_2	σ_2	σ_2	σ_2	σ_2	σ_2	σ_3	σ_3	σ_3	σ_3	σ_3^2	σ_3^2	σ_3^2	σ_3^2	σ_4	σ_4	σ_4	σ_4^3	σ_4^3	σ_4^3	σ_4^2	σ_4^2	σ_4^2	s_2	s_4	s_4	s_4	s_4^3	s_4^3	s_4^3	s_6	s_6	s_6	s_6	s_6^5	s_6^5	s_6^5	s_6^5	h	h	h	d	d	d	d	d	d
		1-7	2-8	3-5	4-6	9-11	10-12	a-a	b-d	c-g	f-h	a-a	b-d	c-g	f-h	i-k	j-l	a-a	i-k	j-l	a-a	i-k	j-l	a-a	i-k	j-l	a-a	i-k	j-l	a-a	a-a	b-d	c-g	f-h	a-a	b-d	c-g	f-h	i-k	j-l	a-a	i-k 9-11	i-k 10-12	a-a 3-5	a-a 1-7	2-6	4-8
r_1	1	1	11	7	12	8	6	9	8	6	10	4	11	12	2	4	10	3	2	9	5	3	5	7	7	8	11	3	6	12	5	6	9	10	8	11	2	4	12	5	3	1	4	8	7	1	9	10
r_2	2	9	2	12	8	7	5	5	9	11	1	12	7	3	10	1	6	11	3	4	10	4	8	6	8	5	6	12	7	4	9	10	1	5	12	3	11	9	7	6	2	4	3	1	11	10	8	2
r_3	3	5	10	3	9	6	8	10	4	2	9	8	12	11	6	2	11	7	4	12	1	1	7	5	5	6	10	7	8	9	1	2	10	9	4	12	6	8	11	7	1	3	2	4	3	5	12	11
r_4	4	10	6	11	4	5	7	1	12	10	5	9	3	7	11	3	2	12	1	8	9	2	4	8	6	7	2	11	5	8	10	11	5	1	9	7	10	12	3	8	4	2	1	3	12	9	4	6
r_5	5	3	12	5	11	4	2	12	6	8	11	2	10	9	4	8	9	1	6	10	7	7	1	3	3	4	12	1	2	11	7	8	12	11	6	10	4	2	9	1	7	5	8	6	5	3	10	9
r_6	6	12	4	9	6	3	1	7	10	12	3	11	5	1	9	5	8	10	7	2	11	8	4	2	4	1	8	9	3	2	12	9	3	7	11	1	12	10	5	2	6	8	7	5	10	11	6	4
r_7	7	7	9	1	10	2	4	11	2	4	12	6	9	10	8	6	12	5	8	11	3	5	3	1	1	2	9	5	4	10	3	4	11	12	2	9	8	6	10	3	5	7	6	8	1	7	11	12
r_8	8	11	8	10	2	1	3	3	11	9	7	10	1	5	12	7	4	9	5	6	12	6	2	4	2	3	4	10	1	6	11	12	7	3	10	5	9	11	1	4	8	6	5	7	9	12	2	8
r_9	9	2	7	6	3	9	11	6	7	5	6	1	2	8	3	12	1	4	10	5	8	11	10	12	11	12	3	2	10	7	6	7	8	2	5	6	1	3	4	9	12	10	9	11	8	4	1	5
r_{10}	10	4	3	8	7	12	10	0	5	7	2	3	1	4	1	9	5	2	11	1	6	12	9	11	12	9	7	4	11	3	8	5	4	6	7	2	3	1	8	10	11	9	12	10	6	2	5	1
r_{11}	11	8	1	4	5	11	9	4	1	3	4	7	8	2	5	10	7	6	12	3	2	9	12	10	9	10	5	8	12	1	4	1	2	8	3	4	7	5	6	11	10	12	11	9	2	6	7	3
r_{12}	12	6	5	2	1	10	12	2	3	1	8	5	4	6	7	11	3	8	9	7	4	10	11	9	10	11	1	6	9	5	2	3	8	4	1	8	5	7	2	12	9	11	10	12	4	8	3	7
s_1	1	-1	-11	-7	-12	-8	-6	9	8	6	10	4	11	12	2	-4	-10	-3	-2	-9	-5	3	5	7	-7	8	11	3	6	12	5	-6	-9	-10	-8	-11	-2	-4	-12	-5	-3	-1	4	8	7	1	9	10
s_2	2	-9	-2	-12	-8	-7	-5	5	9	11	1	12	7	3	10	-1	-6	-11	-3	-4	-10	4	8	6	-8	5	6	12	7	4	9	-10	-1	-5	-12	-3	-11	-9	-7	-6	-2	-4	3	1	11	10	8	8
s_3	3	-5	-10	-3	-9	-6	-8	10	4	2	9	8	12	11	6	-2	-11	-7	-4	-12	-1	1	7	5	-5	6	10	7	8	9	1	-2	-10	-9	-4	-12	-6	-8	-11	-7	-1	-3	2	4	3	5	12	11
s_4	4	-10	-6	-11	-4	-5	-7	1	12	10	5	9	3	7	11	-3	-2	-12	-1	-8	-9	2	4	8	-6	7	2	11	5	8	10	-11	-5	-1	-9	-7	-10	-12	-3	-8	-4	-2	1	3	12	9	4	6
s_5	5	-2	-7	-6	-3	-9	-11	4	7	9	6	1	2	8	3	-12	-1	-4	-10	-5	-8	11	10	12	-11	12	3	2	10	7	6	-7	-8	-2	-5	-6	-1	-3	-4	-9	-12	-10	9	11	8	4	2	5
s_1	1	-1	-11	-7	-12	-8	-6	9	8	6	10	4	11	12	2	-4	-10	-3	-2	-9	-5	3	5	7	7	-8	-11	-3	-6	-12	-5	6	9	10	8	11	2	4	12	5	3	1	-4	-2	-7	-1	-9	-10
s_2	2	-9	-2	-12	-8	-7	-5	5	9	11	1	12	7	3	10	-1	-6	-11	-3	-4	-10	4	8	6	8	-5	-6	-12	-7	-4	-9	10	1	5	12	3	11	9	7	6	2	4	-3	-1	-11	-10	-8	-2
s_3	3	-5	-10	-3	-9	-6	-8	10	4	2	9	8	12	11	6	-2	-11	-7	-4	-12	-1	1	7	5	5	-6	-10	-7	-8	-9	-1	2	10	9	4	12	6	8	11	7	1	3	-2	-4	-3	-5	-12	-11
s_4	4	-10	-6	-11	-4	-5	-7	1	12	10	5	9	3	7	11	-3	-2	-12	-1	-8	-9	2	4	8	-6	7	2	11	5	8	10	-11	-5	-1	-9	-7	-10	-12	-3	-8	-4	-2	1	3	12	9	4	6
s_5	5	-2	-7	-6	-3	-9	-11	4	7	9	6	1	2	8	3	-12	-1	-4	-10	-5	-8	11	10	12	11	-12	-3	-2	-10	-7	-6	7	8	2	5	6	1	3	4	9	12	10	-9	-11	-8	-4	-1	-5

and 10; m by 4, 8, 9, and 12; and n by 2, 6, 10, and 11.

The bonds formed by the overlapping of the sp_z orbitals will be considered first. The reducible representation reduces to

$$A_{2u} + E_u + F_{1g} + F_{1u} + F_{2g} \qquad (28)$$

Since there are 12 atoms, equation (27) will yield 12 linear combinations for each irreducible representation. However, these 12 functions are not independent. In the section on group theory it was shown that the number of eigenfunctions which form a basis for a particular irreducible representation is equal to its dimension. Consequently, the 12 functions obtained for each irreducible representation can be reduced to d_i independent functions which form a basis for the representation. As before, d_i is the dimension of the ith irreducible representation. If the irreducible representation has s_i set of functions which form bases for it, the 12 functions can be reduced to $s_i \times d_i$ independent functions.

Equations (29) are the functions which form bases for the irreducible representations of equation (28).

$$\psi_{r1} = \frac{1}{\sqrt{12}} (r_1 + r_2 + r_3 + r_4 + r_5 + r_6 + r_7 + r_8 + r_9 + r_{10} + r_{11} + r_{12}) \qquad A_{1g}$$

$$\psi_{r2} = \frac{1}{\sqrt{24}} (2r_1 - r_2 + 2r_3 - r_4 + 2r_5 - r_6 + 2r_7 - r_8 - r_9 - r_{10} - r_{11} - r_{12})$$

$$\psi_{r3} = \frac{1}{\sqrt{24}} (r_1 - 2r_2 + r_3 - 2r_4 + r_5 - 2r_6 + r_7 - 2r_8 + r_9 + r_{10} + r_{11} + r_{12}) \qquad E_g$$

$$\psi_{r4} = \frac{1}{4} (2r_1 + r_2 + r_4 - r_6 - 2r_7 - r_8 + r_9 + r_{10} - r_{11} - r_{12})$$

$$\psi_{r5}=\frac{1}{4}(r_1+2r_2+r_3-r_5-r_7-2r_8-r_9+r_{10}+r_{11}-r_{12}) \qquad F_{1u}$$

$$\psi_{r6}=\frac{1}{4}(r_2+2r_3+r_4-2r_5-r_6-r_8-r_9-r_{10}+r_{11}+r_{12}) \qquad (29)$$

$$\psi_{r7}=\frac{1}{2}(r_1-r_3-r_5+r_7)$$

$$\psi_{r8}=\frac{1}{2}(r_2-r_4-r_6+r_8) \qquad F_{2g}$$

$$\psi_{r9}=\frac{1}{2}(r_9-r_{10}+r_{11}-r_{12})$$

$$\psi_{r10}=\frac{1}{4}(2r_1-r_2-r_4+r_6-2r_7+r_8-r_9-r_{10}+r_{11}+r_{12})$$

$$\psi_{r11}=\frac{1}{4}(r_1-2r_2+r_3-r_5-r_7+2r_8-r_9+r_{10}+r_{11}-r_{12}) \qquad F_{2u}$$

$$\psi_{r12}=\frac{1}{4}(-r_2+2r_3-r_4-2r_5+r_6+r_8+r_9+r_{10}-r_{11}-r_{12})$$

Although these d_i functions are independent, they are not, in general, orthogonal. However, the functions which belong to different irreducible representations are orthogonal.

These functions <u>could</u> be used in setting up the 12th order secular determinant obtained by applying the variation method previously mentioned. This determinant is of the form

$$\begin{vmatrix} H_{11}-S_{11}E & H_{12}-S_{12}E & \cdots & H_{1n}-S_{1n}E \\ H_{21}-S_{21}E & H_{22}-S_{22}E & \cdots & H_{2n}-S_{2n}E \\ \vdots & & & \\ H_{n1}-S_{n1}E & H_{n2}-S_{n2}E & \cdots & H_{nn}-S_{nn}E \end{vmatrix} = 0 \qquad (30)$$

where

$$H_{ij}=\int \psi_i H \psi_i \, d\tau \qquad (31)$$

and

$$S_{ij} = \int \psi_i \psi_j \, d\tau \qquad (32)$$

It can be shown that $H_{ij}=0$ only when ψ_i and ψ_j belong to different irreducible representations. It will be assumed that the r's are normalized and orthogonal so that $S_{ij}=0$ when ψ_i and ψ_j do not belong to some irreducible representation. This means that the secular determinant can be broken down into several lower order determinants. The number of determinants will be equal to the number of irreducible representations, and the order of each will be equal to the dimension of the irreducible representation.

The secular determinants can be solved to obtain the energies corresponding to the particular irreducible representation. These values for E_i are then put back into the set of linear homogeneous equations, and the values for the coefficients of the approximate wave function obtained.

This last step is not necessary if group theory is used, as in this problem. The functions which form bases for the irreducible representations are obtained directly from the group theory. Consequently, if some other method of finding the proper E_i values could be found, it would not be necessary to use the variation method at all.

This can be done quite simply. Schrödinger's equation can be written

$$H\psi_i = E_i \psi_i \qquad (33)$$

where ψ_i is an eigenfunction of the ith irreducible representation with eigenvalue E_i. Multiply both sides by ψ_i and integrate over the region where ψ_i has a finite value.

$$\int \psi_i H \psi_i \, d\tau = E_i \int \psi_i \psi_i \, d\tau \tag{34}$$

and

$$E_i = \frac{\int \psi_i H \psi_i \, d\tau}{\int \psi_i \psi_i \, d\tau} \tag{35}$$

If the ψ_i are normalized

$$E_i = \int \psi_i H \psi_i \, d\tau \tag{36}$$

This would require that the r_1 functions be orthogonal. If they are not orthogonal, the energy level from equation (36) would be divided by a constant. Nevertheless, the energy levels will still be expressed in terms of the same integrals. For the sake of simplicity, it will be assumed that r_1 functions are orthogonal. The same assumption will be made for the p_x and p_y orbitals.

Equation (35) indicates that it is only necessary to know one of the functions from each irreducible representation to calculate the energy level corresponding to that representation. When there is only one set of functions forming a basis for each irreducible representation the problem can be solved in this manner, so that it is not necessary to use the variation method. This is true for the cuboctahedral structure since the total number of atomic orbitals is equal to the sum of the dimensions of the irreducible representations.

If any irreducible representation has more than one

set of functions which form bases for it, the problem becomes more complicated. Each set of functions are degenerate, but the two sets have different eigenvalues. If there are two sets of functions, there will be two energy levels corresponding to this representation.

Equation (27) does not yield the two sets directly, but linear combinations of the functions forming the two bases will be obtained. It will then be necessary to use the variation method to determine the energy levels and the coefficients of the linear combinations obtained from the group theory.

It should be pointed out that the energy levels for the other representations can still be obtained in the manner previously discussed. It will only be necessary to use the variation method on the one irreducible representation which has more than one set of basis functions. This means it would be necessary to solve a $s_j \times d_j$ secular determinant whenever s_j is greater than one.

Judging from the approximations made by Lipscomb and Britton, it seems that they did not reduce the secular determinant in the manner described above but made several simplifying approximations and solved the 12th order determinant. In their approximations they assumed that all of the H_{ij} functions were zero except those involving nearest neighbors in the p_y bonds. These approximations were obviously not made in the sp_z bonding since the energies are

given in terms of integrals between all of the neighbors in the structure. The energies for the sp_z orbitals are expressed in terms of the integrals H_o, α, β, γ, and δ. These integrals are of the form

$$\int r_i H r_i \, d\tau \qquad (37)$$

where $i=j$ for H_o, i and j represent nearest neighbors in α, second nearest neighbors in β, third nearest neighbors in γ, and fourth nearest neighbors in δ. All of these integrals, except H_o, are called resonance integrals. These integrals exist because there is a finite probability of finding a bonding electron from one atom in any of the bonding orbitals between this and all other atoms in the molecule. The electrons are thought of as spending a fraction of their time in all of the bonding orbitals.

Bonding among the sp_z orbitals will be considered first. The energy E_i of any irreducible representation can be found by using any one of the functions of the representation in equation (35). These energy levels for the sp_z orbitals are

A_{1g}:	$H_o + 4\alpha + 2\beta + 4\gamma + \delta$	bonding	
E_g:	$H_o - 2\alpha + 2\beta - 2\gamma + \delta$	antibonding	
F_{1u}:	$H_o + 2\alpha - 2\gamma - \delta$	bonding	(38)
F_{2g}:	$H_o - 2\beta + \delta$	antibonding	
F_{2u}:	$H_o - 2\alpha + 2\gamma - \delta$	antibonding	

These are the same as the levels found by Lipscomb and Britton.

In a similar fashion, the bonding among p_x and p_y orbitals can be discussed. The σ'_x reducible representation for the p_x orbitals reduces to

$$A_{2u} + E_u + F_{1g} + F_{1u} + F_{2g} \qquad (39)$$

Equations (40) are the functions which form bases for these irreducible representations.

$$\psi_{t1} = \frac{1}{\sqrt{12}} (t_1 + t_2 + t_3 + t_4 + t_5 + t_6 + t_7 + t_8 + t_9 + t_{10} + t_{11} + t_{12}) \qquad A_{2u}$$

$$\psi_{t2} = \frac{1}{\sqrt{24}} (2t_1 - t_2 + 2t_3 - t_4 + 2t_5 - t_6 + 2t_7 - t_8 - t_9 - t_{10} - t_{11} - t_{12}) \qquad E_u$$

$$\psi_{t3} = \frac{1}{\sqrt{24}} (-t_1 + 2t_2 - t_3 + 2t_4 - t_5 + 2t_6 - t_7 + 2t_8 - t_9 - t_{10} - t_{11} - t_{12})$$

$$\psi_{t4} = \frac{1}{4} (2t_1 - t_2 - t_4 + t_6 - 2t_7 + t_8 - t_9 - t_{10} + t_{11} + t_{12})$$

$$\psi_{t5} = \frac{1}{4} (-t_1 + 2t_2 - t_3 + t_5 + t_7 - 2t_8 + t_9 - t_{10} - t_{11} + t_{12}) \qquad F_{1g}$$

$$\psi_{t6} = \frac{1}{4} (-t_2 + 2t_3 - t_4 - 2t_5 + t_6 + t_8 + t_9 + t_{10} - t_{11} - t_{12}) \qquad (40)$$

$$\psi_{t7} = \frac{1}{2} (t_1 - t_3 - t_5 + t_7)$$

$$\psi_{t8} = \frac{1}{2} (t_2 - t_4 - t_6 + t_8) \qquad F_{1u}$$

$$\psi_{t9} \frac{1}{2} (t_9 - t_{10} + t_{11} - t_{12})$$

$$\psi_{t10} \frac{1}{4} (2t_1 + t_2 + t_4 - t_6 - 2t_7 - t_8 + t_9 + t_{10} - t_{11} - t_{12})$$

$$\psi_{t11} = \frac{1}{4} (t_1 + 2t_2 + t_3 - t_5 - t_7 - t_8 - t_9 + t_{10} + t_{11} - t_{12}) \qquad F_{2g}$$

$$\psi_{t12} = \frac{1}{4} (t_2 + 2t_3 + t_4 - 2t_5 - t_6 - t_8 - t_9 - t_{10} + t_{11} + t_{12})$$

There are only five t_i functions listed in Table III. It was found that this was all that was needed to form bases for all of the irreducible representations in equation (39). Different sets of linearly independent functions could have

been found which would also have formed bases for these representations. However, they would yield the same energy levels.

The eigenvalues are found in the same manner as for the sp_z orbitals and are

A_{2u}:	$H_o+4\epsilon-2\varsigma-4\eta+\theta$	bonding
E_u:	$H_o-2\epsilon-2\varsigma+2\eta+\theta$	antibonding
F_{1g}:	$H_o-2\epsilon-2\eta-\theta$	antibonding (41)
F_{1u}:	H_o	nonbonding
F_{2g}:	$H_o+2\epsilon+2\eta-\theta$	bonding

The parameters ϵ, ς, η, and θ represent resonance integrals between nearest, 2nd nearest, 3rd nearest, and 4th nearest neighbors, respectively.

The signs have been adjusted so all of the parameters are negative. The orientation of the orbitals in Figure 1 must be considered to determine which signs must be changed. If the portions of the two functions which extend toward each other have the same sign, there will be a high probability of finding the electrons between the two nuclei. This results in attraction between the two nuclei which strengthens the bonding. Since the bonding is stronger, the molecule is at a lower energy. This means that the integral is already negative so no sign change is necessary. If the portions which extend toward each other have opposite signs, a nodal surface is introduced between the atoms involved. This means a low probability of finding the elec-

trons between the nuclei. This results in a repulsion between nuclei, and the bonding is weakened. Consequently, the integral is positive, and the sign must be changed since all integrals are considered negative.

The problem of determining the proper sign of the integrals did not arise in dealing with the sp_z orbitals since the portions of the orbitals interior to the structure all have the same sign, and the integrals are all negative. However, in dealing with the p_x and p_y orbitals the signs of the integrals will have to be determined.

The signs of the integrals in the p_x energy levels are obtained by considering the orientations of these orbitals. They are oriented so the portions of all three orbitals pointing toward the center of each triangle have the same sign. Consequently, ϵ and θ were negative, and S and η were positive before the signs were changed.

Bonding among the p_y orbitals can also be considered in a similar fashion. The σ'_y reducible representation in Table II reduces to

$$A_{2g} + E_g + F_{1g} + F_{1u} + F_{2u} \qquad (42)$$

Only the four t_1 functions listed in Table III are necessary to find bases of these representations. Equations (43) are the functions which form these bases.

$$\psi_{s1} = \frac{1}{\sqrt{12}} (s_1 + s_2 + s_3 + s_4 + s_5 + s_6 + s_7 + s_8 + s_9 + s_{10} + s_{11} + s_{12}) \qquad A_{2g}$$

$$\psi_{s2} = \frac{1}{\sqrt{24}} (2s_1 - s_2 + 2s_3 - s_4 + 2s_5 - s_6 + 2s_7 - s_8 - s_9 - s_{10} - s_{11} - s_{12})$$

$$\psi_{s3} = \frac{1}{\sqrt{24}} (-s_1 + 2s_2 - s_3 + 2s_4 - s_5 + 2s_6 - s_7 + 2s_8 - s_9 - s_{10} - s_{11} - s_{12}) E_g$$

$$\psi_{s4} = \frac{1}{2} (s_1 - s_3 - s_5 + s_7)$$

$$\psi_{s5} = \frac{1}{2} (s_2 - s_4 - s_6 + s_8) \qquad F_{1g}$$

$$\psi_{s6} = \frac{1}{2} (s_9 - s_{10} + s_{11} - s_{12})$$

(43)

$$\psi_{s7} = \frac{1}{4} (2s_1 - s_2 - s_4 + s_6 - 2s_7 + s_8 - s_9 - s_{10} + s_{11} + s_{12})$$

$$\psi_{s8} = \frac{1}{4} (-s_1 + 2s_2 - s_3 + s_5 + s_7 - 2s_8 + s_9 - s_{10} - s_{11} + s_{12}) \qquad F_{1u}$$

$$\psi_{s9} = \frac{1}{4} (-s_1 + s_2 + s_3 - s_4 - s_5 + s_6 + s_7 + s_8 + 2s_9 - 2s_{11})$$

$$\psi_{s10} = \frac{1}{\sqrt{12}} (2s_1 + s_2 + s_4 - s_6 - 2s_7 - s_8 + s_9 + s_{10} - s_{11} - s_{12})$$

$$\psi_{s11} = \frac{1}{\sqrt{12}} (s_1 + 2s_2 + s_3 - s_5 - s_7 - 2s_8 - s_9 + s_{10} + s_{11} - s_{12}) \qquad F_{2u}$$

$$\psi_{s12} = \frac{1}{\sqrt{12}} (s_1 - s_2 - s_3 + s_4 + s_5 + s_6 + s_7 + s_8 + 2s_9 - 2s_{11})$$

The eigenvalues corresponding to these functions are

A_{2g}:	$H_o - 4\iota + 2K - 4\lambda - \mu$	antibonding	
E_g:	$H_o + 2\iota + 2K + 2\lambda - \mu$	bonding	
F_{1g}:	$H_o - 2K - \mu$	antibonding	(44)
F_{1u}:	$H_o + 2\iota - 2\lambda + \mu$	bonding	
F_{2u}:	$H_o - 2\iota + 2\lambda + \mu$	antibonding	

The integrals ι, K, λ, and μ represent resonance integrals between nearest, 2nd nearest, 3rd nearest, and 4th nearest neighbors, respectively. Lipscomb and Britton represent ι and K by ζ and η, respectively.

The p_y orbitals are oriented in such a manner that the portions of orbitals which point toward the center of

the squares from opposite corners have the same sign. There are two positive and two negative contributions in each square. Consequently, ι, λ, and μ were positive, and K was negative before the signs were changed.

All of the energy levels have been labeled as bonding, nonbonding, or antibonding. The levels that produce bonding, arranged in order of increasing stability after the triply degenerate, nonbonding one, are

$$\begin{aligned}
&\Sigma t, \quad F_{1u}(3): && H_0 \\
&\Sigma r, \quad F_{1u}(3): && H_0+2\alpha+0\beta-2\gamma-\delta \\
&\Sigma s, \quad F_{1u}(3): && H_0+2\iota+0K-2\lambda+\mu \\
&\Sigma t, \quad F_{2g}(3): && H_0+2\epsilon+0\varsigma+2\eta-\theta \\
&\Sigma s, \quad E_g(2): && H_0+2\iota+2K+2\lambda-\mu \\
&\Sigma t, \quad A_{2u}(1): && H_0+4\epsilon-2\varsigma-4\eta+\theta \\
&\Sigma r, \quad A_{1g}(1): && H_0+4\alpha+2\beta+4\gamma+\delta
\end{aligned} \tag{45}$$

The additional terms which have been introduced do not alter the essential conclusions of Lipscomb and Britton. However, it is apparent, in this case at least, that the use of group theory simplified the problem considerably and yielded more complete results than the method used by Lipscomb and Britton. Also, it seems very possible that there would be times when the resonance integrals neglected by them would determine whether an energy level was bonding or antibonding. These considerations, plus the added insight into the problem, makes the method used here a desirable one.

MOLECULAR ORBITAL BONDING IN THE ICOSAHEDRAL STRUCTURE

Since the icosahedral structure can be obtained by small distortions of the cuboctahedron, it would be of some interest to consider the molecular orbital bonding in this structure.

It can be represented as 12 atoms at the vertices of an icosahedron, or 12 atoms at the centers of the faces of a dodecahedron. The latter method is chosen here.

The same sets of orbitals, sp_z, p_x, and p_y, will be considered here as for the cuboctahedron.

One set of sp_z orbitals are again directed toward the center of the structure, and the external set is ignored. The same method as used for the cuboctahedron in determining the molecular orbitals and the energy levels is followed here.

Table IV shows the results of operating on all 12 sp_z orbitals with the operations of the I group, the symmetry group of the icosahedral structure.

The C_5, C_5^2, C_5^3, and C_5^4 operations represent counterclockwise rotations of 72, 144, 216, and 288 degrees, respectively, about axes through the centers of opposite faces of the dodecahedron. The C_2 operation represents a counterclockwise rotation of 180 degrees about axes through the middle of opposite edges. The C_3 and C_3^2 operations represent rotations of 120 and 240 degrees, respectively, about axes through opposite vertices.

TABLE IV. APPLICATION OF THE I GROUP OPERATIONS TO ω_2 ORBITALS.

The number of each face appears on Figure 2. The solid circles represent atoms on upper faces; the open circles those on lower faces. The vertices are represented by small letters, and the edges by capital letters. The vertices and edges are not labeled on the figure.

The vertices of the top face, starting with the one nearest to the number 10 and proceeding in counterclockwise direction, are a, b, c, d, and e. The vertices of the bottom face, starting with the one nearest the number 2 and proceeding in counterclockwise direction are p, q, r, s, and t. The rest of the vertices, starting with the one which the x-axis appears to pass through, and proceeding in counterclockwise direction, are k, f, l, g, m, h, n, i, o, and j. The edges connecting vertices a and b, b and c, c and d, d and e, and e and a are A, B, C, D, and E, respectively. The edges connecting vertices a and j, b and f, c and g, d and h, and e and i are J, F, G, H, and I, respectively. The edges connecting vertices p and k, q and l, r and m, s and n, and t and o are K, L, M, N, and O, respectively. Finally, the edges connecting vertices k and f, f and l, l and g, g and m, m and h, h and n, n and i, i and o, o and j, and j and k are P, Q, R, S, T, U, V, W, X, and Y, respectively.

The reducible representation for the sp_z orbitals is the same as the σ representation for central atom bonding in this structure. This representation and its irre-

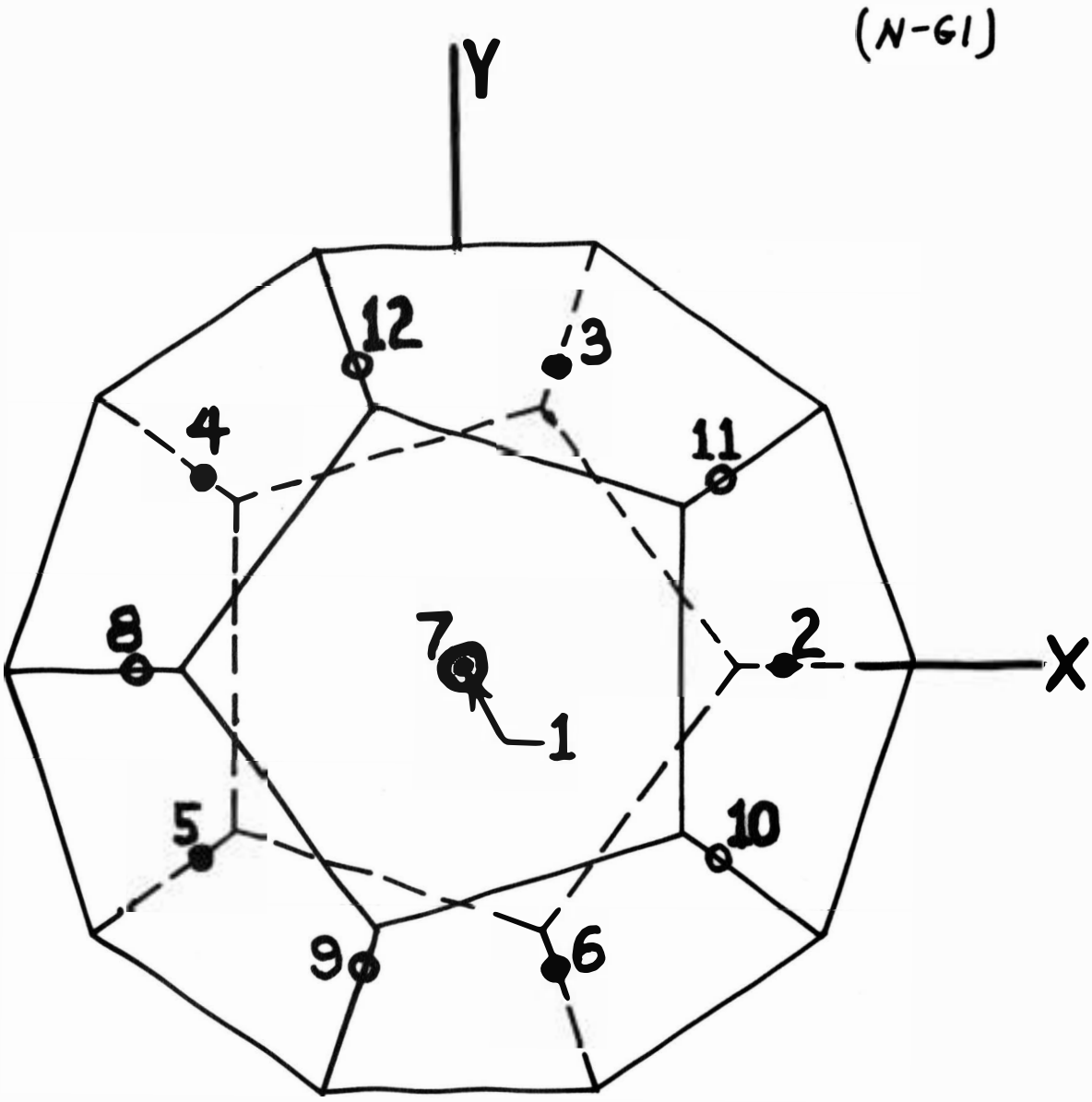

Figure 2. Location of Atoms at Face Centers of a Regular Dodecahedron Pierced Symmetrically by Coordinate Axes. The Solid Circles Represent Atoms on Upper Faces; the Open Circles Those on Lower Ones.

reducible components are obtained from Macek and Duffey's paper[34]. The irreducible representations are

$$A + F_1 + F_2 + H \tag{46}$$

The functions which form bases for these irreducible representations are determined by using the results of Table IV and equation (27). These functions are

$$\psi_{r1} = \frac{1}{\sqrt{12}}(r_1+r_2+r_3+r_4+r_5+r_6+r_7+r_8+r_9+r_{10}+r_{11}+r_{12}) \quad A$$

$$\psi_{r2} = \frac{1}{\sqrt{20}}(r_1+\sqrt{5}r_2+r_3-r_4-r_5+r_6-r_7-\sqrt{5}r_8-r_9+r_{10}+r_{11}-r_{12})$$

$$\psi_{r3} = \frac{1}{\sqrt{20}}(r_1+r_2+\sqrt{5}r_3+r_4-r_5-r_6-r_7-r_8-\sqrt{5}r_9-r_{10}+r_{11}+r_{12}) \quad F_1$$

$$\psi_{r4} = \frac{1}{\sqrt{20}}(r_1-r_2+r_3+\sqrt{5}r_4+r_5-r_6-r_7+r_8-r_9-\sqrt{5}r_{10}-r_{11}+r_{12})$$

$$\psi_{r5} = \frac{1}{\sqrt{20}}(-r_1+\sqrt{5}r_2-r_3+r_4+r_5-r_6+r_7-\sqrt{5}r_8+r_9-r_{10}-r_{11}+r_{12})$$

$$\psi_{r6} = \frac{1}{\sqrt{20}}(-r_1-r_2+\sqrt{5}r_3-r_4+r_5+r_6+r_7+r_8-\sqrt{5}r_9+r_{10}-r_{11}-r_{12}) \quad F_2$$

$$\psi_{r7} = \frac{1}{\sqrt{20}}(-r_1+r_2-r_3+\sqrt{5}r_4-r_5+r_6+r_7-r_8+r_9-\sqrt{5}r_{10}+r_{11}-r_{12}) \tag{47}$$

$$\psi_{r8} = \frac{1}{\sqrt{60}}(\sqrt{5}r_1-r_2-r_3-r_4-r_5-r_6+\sqrt{5}r_7-r_8-r_9-r_{10}-r_{11}-r_{12})$$

$$\psi_{r9} = \frac{1}{\sqrt{60}}(-r_1+\sqrt{5}r_2-r_3-r_4-r_5-r_6-r_7+\sqrt{5}r_8-r_9-r_{10}-r_{11}-r_{12})$$

$$\psi_{r10} = \frac{1}{\sqrt{60}}(-r_1-r_2+\sqrt{5}r_3-r_4-r_5-r_6-r_7-r_8-\sqrt{5}r_9-r_{10}-r_{11}-r_{12}) \quad H$$

$$\psi_{r11} = \frac{1}{\sqrt{60}}(-r_1-r_2-r_3+\sqrt{5}r_4-r_5-r_6-r_7-r_8-r_9+\sqrt{5}r_{10}-r_{11}-r_{12})$$

$$\psi_{r12} = \frac{1}{\sqrt{60}}(-r_1-r_2-r_3-r_4+\sqrt{5}r_5-r_6-r_7-r_8-r_9-r_{10}+\sqrt{5}r_{11}-r_{12})$$

Since the sum of the dimensions of the irreducible representations in equation (46) is equal to the total num-

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[34]Joseph H. Macek and George H. Duffey, op. cit.

ber of atomic orbitals available, there will be only one set of functions forming a basis for each irreducible representation. This means that the four energy levels can be found by substituting one function from each representation into equation (36). It will not be necessary to solve a secular determinant.

The energy levels of these irreducible representations are

$$\begin{aligned} &A: && H_0 + 5\alpha + 5\beta + \gamma && \text{bonding} \\ &F_1: && H_0 + \sqrt{5}\alpha + \sqrt{5}\beta - \gamma && \text{bonding} \\ &F_2: && H_0 - \sqrt{5}\alpha - \sqrt{5}\beta - \gamma && \text{nonbonding} \\ &H: && H_0 - \alpha - \beta + \gamma && \text{nonbonding} \end{aligned} \tag{48}$$

In these expressions α, β, and γ represent resonance integrals between nearest, second nearest, and third nearest neighbors, respectively. The signs of these integrals are all negative since the portions which overlap all have the same sign.

The bonding and nonbonding properties of the orbitals were determined in the same manner as for the cuboctahedron.

It would now be desirable to determine the energy levels of the p_x and p_y orbitals in the same manner as in the cuboctahedron. It quickly becomes apparent that this is going to be a much more complicated problem because of the type of symmetry. It will be recalled that in the cuboctahedron the p_x and p_y orbitals of one atom always transformed into a p_x or p_y orbital, respectively, of another

atom. In other words, the symmetry of the structure made the choice of orienting the p_x and p_y orbitals obvious. This is not the case in the icosahedral structure. No obvious orientation of the orbitals will make it possible to transform them into like orbitals of another atom under the operations of the group. The result is that the p_x and p_y orbitals transform into linear combinations of each other regardless of their orientation. Consequently, these two sets of orbitals have to be treated together in determining the molecular orbitals in this manner. Theoretically, this still does not present a problem. However, the time involved in determining all the linear combinations would be great.

Since the method used for the sp_z orbitals presents such a problem, it would be desirable to find some other way of determining the p_x and p_y energy levels.

The first alternative considered was the variation method. The p_x and p_y orbitals could be treated individually, but it would require solving a 12th order determinant for each set of functions unless a way of reducing this determinant could be found. Following the procedure used by Lipscomb and Britton, all of the resonance integrals except those between nearest neighbors were neglected. It was hoped that this would allow one to reduce the determinant. Unfortunately, it did not accomplish this objective.

Another possibility for solving the 12th order deter-

minants would be to use the IBM 1620 computer being obtained by the Engineering Division. The computer handles only numerical problems, which ordinarily would require knowing the values for all of the integrals. However, in this case it seems that results might be obtained without evaluating the integrals. A parameter could be assigned to each integral, and these parameters varied one at a time, holding the others constant, until the minimum values for the energy levels were obtained on solving the secular determinant.

This would probably involve a large number of calculations; but with a computer, it would be feasible.

Besides the above methods, one might use a method discussed briefly by Mulliken[35]. Here it would involve correlating the irreducible representations of the icosahedral structure with those of the cuboctahedral structure which have been solved. The results would not be as complete as might be obtained from the previously discussed methods, but could furnish some information.

The difficulties involved in this structure seem to arise because of the lack of "right angle" symmetry. The p_x and p_y orbitals of different atoms must be parallel or oriented at right angles to each other for all rotations about symmetry axes to effect a one-to-one transformation--

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[35] R.S. Mulliken, Phys. Rev. 43, 279, 1932.

that is, one orbital into only one other one.

CONCLUSIONS

The wave functions involved in the central atom bonding in the cuboctahedral structure have been obtained. The Pauling strengths of these bonds were calculated, and compared to those in the icosahedral structure. It was concluded that the icosahedral structure would be favored unless the energy of the f-orbitals was quite low, since the strength of the icosahedral bonds with no f-orbital contribution was equal to the maximum bond strength of the cuboctahedral, which occurred with 3.380 f-orbital contribution. The cuboctahedral structure would be favored if the interactions between the ligands are such that they attract, since they are closer together in this structure.

The possible types of π bonding were also discussed. It was determined that all of the π bonds would be weak except those involving the f_β orbitals which were not used in the σ bonding.

The molecular orbitals for the cuboctahedral structure involving no central atom were also obtained. The energy levels for these orbitals were found and compared with those obtained by Lipscomb and Britton. Although more detailed results were obtained here, they did not change their conclusions. However, it did seem that the method used here simplified the problem considerably.

The molecular orbital method was also discussed as it applied to the icosahedral structure. The molecular or-

bitals and energy levels were obtained for the sp_z orbitals in the same manner as for the cuboctahedral structure. However, complications developed when the p_x and p_y orbitals were considered. The difficulties encountered here seemed to stem from the fact that the icosahedral structure lacked the "right angle" symmetry of the cuboctahedral structure.

These problems were discussed and possible solutions suggested. The most promising possibility seems to be in making use of the IBM 1620 computer.

The author hopes that it will be possible for someone else to investigate this matter further in connection with the National Science Foundation research program.

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